much closer in the krypton atom than in the nitrogen molecule. A similar statement holds for the bromine and cyanogen molecules, in which the numbers of electrons are 70 and 26 respectively, yet the collision areas are nearly identical,—1·28 as compared with 1·31.

I wish to express my appreciation of the valuable assistance given by Mr. C. J. Smith, of this Department, in the preparation and manipulation of the gas used in these experiments.

The Properties and Molecular Structure of Thin Films of Palmitic Acid on Water. Part I.

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The experiments to be described in this paper have been undertaken in order to obtain confirmation of the very interesting views put forward by Langmuir (1) upon the arrangement of the molecules of various substances spread upon the surface of water. The study of these films has been carried on by a number of workers for many years, some of the principal publications being those of Miss Pockels (2), Rayleigh (3, 4), Hardy (5), Devaux (6), and recently Labrouste (7): but in most of these papers the authors do not enter into much detail regarding the molecular structure of the films.

So much information is now available however as to the dimensions of molecules and the forces about them, much of it being of an accurate quantitative nature, derived from structural organic chemistry, from the study of crystals, the kinetic theory of gases and the deviations from the simple gas laws, etc., that an attempt to deduce the arrangement of the constituent molecules from the properties of the films has become something more than a speculation and may be made with some certainty and definiteness.

And conversely, since the films of fatty acids and the other substances investigated appear to be only one molecule in thickness and to have all the molecules arranged in similar orientation—often simply perpendicular to the surface—measurement of the mechanical properties of films consisting of a known number of molecules of a pure substance, affords unusually direct information concerning the force fields round individual molecules. An accurate knowledge of these fields of force is of fundamental importance, not only to Physics but to practically all problems of Chemistry, including such as the nature of organic reactions, the theory of solution, and the questions of adsorption and colloidal stability.

Langmuir (*loc. cit.*) brings a great deal of evidence to show that the same force fields are the cause of chemical combination in its widest sense and of cohesion and surface-tension phenomena. This idea is confirmed in a remarkable manner by his experiments upon thin films of various insoluble fatty acids, esters, and alcohols, spread upon water. The molecules of such substances attach themselves to the water by those atomic groups which exhibit residual polar affinity in the reactions of organic chemistry. Thus the saturated fatty acids are attached by their carboxyl groups, the unsaturated acids having additional points of attachment at the ethylenic linkages in the hydrocarbon chain. This definite localization of the points of attraction in the molecule produces an orientation, the palmitic acid molecule turning perpendicular to the surface: while oleic acid, being attached by the carboxyl and also at a point in the middle of the chain, is bent down towards the water at the latter point.

Experimental Method.

The principle of the method of measuring the film's tendency to spread on water is the same as that first used by Miss Pockels, and later by Rayleigh and Hardy. A small measured quantity of the substance dissolved in a volatile solvent is placed on the cleaned surface of water: this spreads at once and evaporates in a few seconds, leaving a film behind. The area available for the film is now contracted gradually by moving barriers along the surface of the water, and the forces on the film are measured.

The compressive force on the film, *i.e.*, the difference between the surface tension of the film and that of pure water, has been measured directly by means of an apparatus similar to Langmuir's (*loc. cit.*, fig. 6), a thin strip of paraffined copper being used as the floating barrier instead of paper. The force on this float was measured by a simple balance. The clearance between the ends of the float and the sides of the trough was 1–2 mm., and escape of the film past the float was prevented by air blasts from two fine jets carefully adjusted in position, as in Langmuir's experiments. These air blasts did not affect the film much except for a very small area near the float, nor was the balance disturbed except for a slight alteration of zero.

I have used an accurately made brass trough measuring 60 by 14·00 by 1·8 cm., the sides being nearly 1 cm. thick and machined and scraped flat on the top. The barriers used for confining the film were strips of window glass about

30 by 1·5 by 0·7 cm.: these rested on the sides of the trough and projected some distance so that they could be handled with little risk of grease spreading from the fingers to the water surface. The trough was filled to the brim and levelled on a separate table.

Precautions necessary in Cleaning and Using the Trough.

It was cleaned with fine emery cloth under the tap until it wetted all over: the barriers were kept in a basin of hot chromic acid, being removed with tongs and washed with hot water so as to dry at once. The trough was dried in a warm place and the top of the sides coated with paraffin wax dissolved in benzene: the under side of the barriers was also coated with wax.

A simple trough of tin plate with paper barriers similar to that used by Langmuir was tried, but the barriers in my hands proved leaky and troublesome to keep in position: the above arrangement appeared capable of giving more accurate results. Water will spread over a clean metal surface and it is therefore difficult or impossible to obtain barriers quite free from leaks if glass and metal surfaces alone are used; the object of the wax was to prevent spreading, and it was found to be quite effective (with careful working) in preventing leaks. Films have been maintained unchanged in area for several hours, under compression.

Accidental leakage occurred occasionally however and was generally due to one of the following causes: the air blasts were not properly adjusted or the edges of the float had become wet so that the effective channels past the ends of the float were more than 2 mm. wide; leaks at the glass barrier were more frequent however and were usually due to the paraffin wax having been partially rubbed off.

Freshly paraffined surfaces rarely gave any trouble.

Residual Contamination.

Perfectly clean water surfaces were not obtained: on the cleanest the float would move away from the barrier at 0·5 cm. distance, after the barrier had been moved from about 35 cm., with a weight in the balance pan of 0·05 grm. Part of this apparent contamination was due to the capillary curvature of the liquid surface in contact with the barriers. Surfaces with more than 1·2 cm. of contamination have not been used.

A clean atmosphere is essential for these experiments: work next door to a laboratory where much organic preparation was being carried on was found impossible, owing to the rapidity with which the surfaces became contaminated.

A correction was made for the contamination as follows: A blank experiment, made immediately prior to putting on the film, gave the total amount of contamination at 0·05 grm., and the compression curve obtained with the film which had accumulated when a clean surface was exposed to the air for some time gave the ratio of the area filled by the contamination at any force to the area at 0·05 grm.

This area was then subtracted from the observed area of a film of palmitic acid. Table I gives some corrections for a commonly occurring amount of contamination.

Table I.—Corrections to Area of Film for Residual Contamination.

Grm. in pan.	Correction (cm. length of trough).	Grm. in pan.	Correction (cm. length of trough).
0·05	0·75	0·5	0·25
0·1	0·63	0·75	0·15
0·2	0·43	1·0	0·08
0·35	0·33		

The amount of contamination is small, but, owing to its much greater compressibility, the correction to the slope of curves of palmitic acid is appreciable. The films used were usually between 20 cm. and 30 cm. in length.

About five drops of benzene were used in putting on a film, and the residue left by this quantity was negligibly small, being certainly not greater than 0·16 cm., and probably much less even than this. The benzene was free from thiophene, was distilled and collected over ½° C., and was finally purified from grease by redistillation in an apparatus free from cork or rubber.

The water was distilled from tap-water in a large copper vessel and condensed in glass, all joints in the still being either ground or cemented with sodium silicate and plaster of Paris.

The palmitic acid was Kahlbaum's K quality, recrystallised from aqueous alcohol. It melted at 62·5° C. The curves show its freedom from unsaturated substances.

The quantity of solution put on the surfaces was measured by counting drops from a capillary pipette. The method is accurate within 3 to 5 per cent., and seems to be much more exact than any other simple method of measuring the small volumes.

The acidity of the water has been controlled by dissolving "buffer" salts in it, the concentration never exceeding M/65, which was generally enough to maintain the P_H* constant within 0·2 unit or nearer throughout a day's exposure.

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* P_H of x denotes a hydrogen ion concentration of 10^{-x}.

The actual P_H was determined by colorimetric comparison with the standards of Clark and Lubs (8), which were checked against a hydrogen electrode.

Comparison experiments on distilled water indicated that these salts in the dilutions employed had little, if any, effect on the films, beyond regulating the hydrogen ion concentration.

$6{\cdot}06 \times 10^{-23}$ has been taken as the Avogadro constant.

Range of Temperature.

The profound change in the films with rising temperature described by Labrouste (7) was ascertained not to occur on any of the solutions investigated until the temperature had risen well above 20° C.

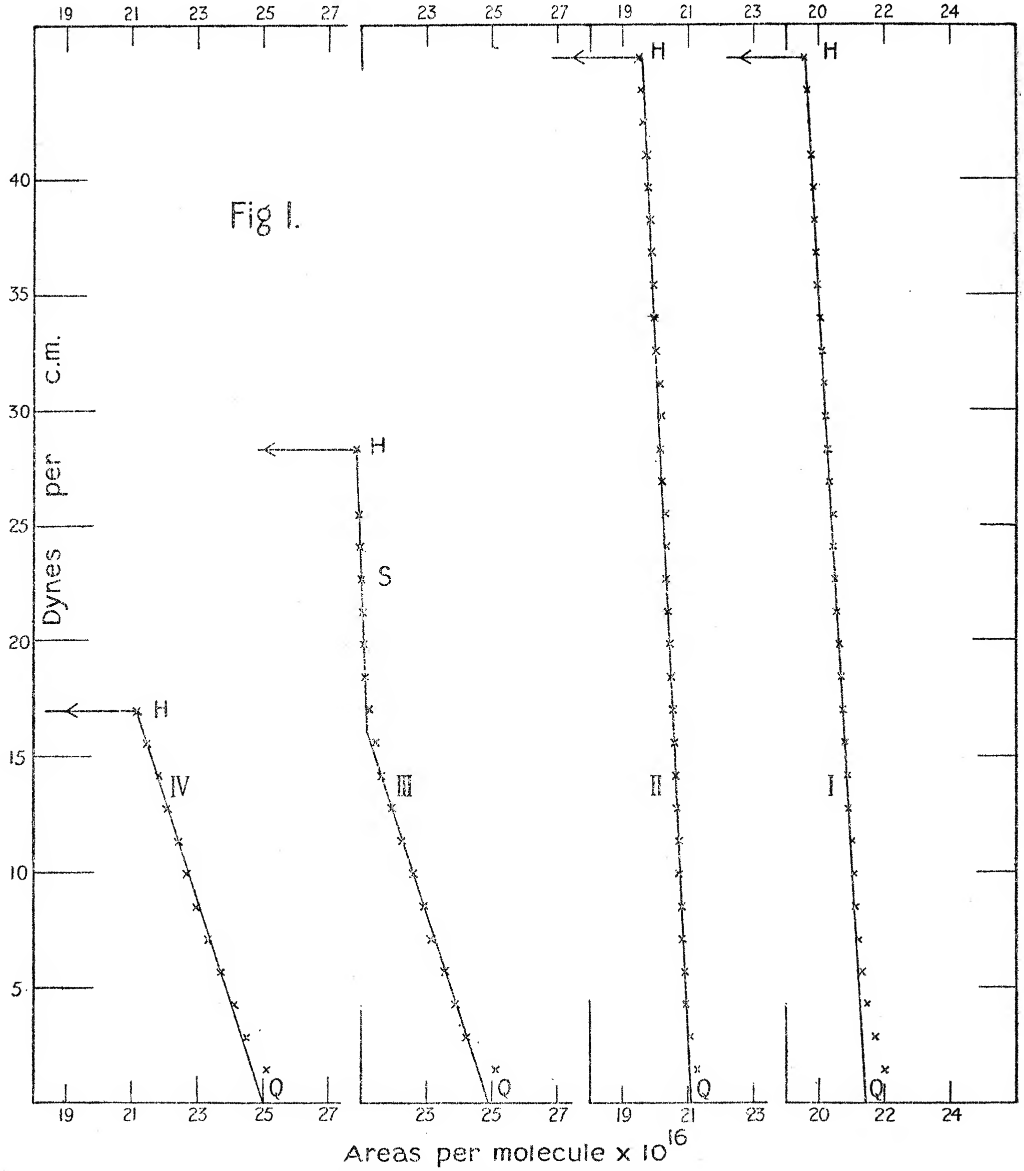
No measurable change occurred between 10° and 20°, and all the experiments described were done within this range, except where specially mentioned.

Discussion of the Curves.

Fig. 1 gives the uncorrected, I, and corrected, II, curves relating the force of compression to the area per molecule on solutions having a P_H between about 8 and 5·5. At areas greater than about 22×10^{-16} sq. cm. per molecule there was no measurable resistance to compression. At this point there was a sudden opposition to further contraction, and the compressive force increased practically linearly with decreasing area. The slope of this line gives the force required for 1 per cent. decrease in area as 5·9 dynes per centimetre: if the density of the material of the film is unity, its thickness is $2{\cdot}11 \times 10^{-7}$ cm., and the force required for 1 per cent. contraction, calculated on 1 sq. cm. cross-section, is 28 megabars. This slope is constant in successive experiments within about 15 per cent., which is probably the error of experiment. It is considerably steeper than the slope of the curves given by Langmuir (*loc. cit.*, fig. 8) for palmitic acid.

The value of the compressibility of the paraffin $C_{15}H_{32}$ obtained from Landolt Börnstein's tables indicates that a force of 125 megabars is required to compress this substance by 1 per cent. of its volume. This force is about 4·5 times as great as for the thin film, the latter being free to expand in thickness during compression.

The co-ordinates of the point H, at which collapse of the film was first detected, were not found susceptible of accurate determination, values from 20 to 45 dynes per centimetre being obtained. There are 95 and 214 megabars respectively. It appeared that the breakdown of a film might be delayed considerably beyond the point at which there would be equilibrium between a film and the substance in bulk on the water. A discussion of the probable reason for this metastable condition will be given later. The values for the force at H are much lower than those given by Langmuir.



From the considerations advanced by Hardy ((5), 1912, p. 319), the probable value for the compression at which a film is in equilibrium with the acid in bulk resting on the surface is about 25 dynes per centimetre near the neutral point.

Effect of Acid. (Fig. 1, III and IV.)

When the hydrion concentration exceeded a point about $P_H = 5{\cdot}5$, the corrected curves became two straight lines, the upper portion being coincident within the error of experiment with the curve on neutral solutions, and the lower being of less steep slope and cutting the axis of no force at about $25{\cdot}2 \times 10^{-16}$ sq. cm. The intersection of the two lines was at about 15 dynes per centimetre at P_H of 5. The change of zero area was completed within a narrow range of P_H; but further increase of acid raised the point of intersection slightly, to about 19 dynes per centimetre, at a P_H of 3.

Physical State of the Films.

Motes on the surface gave (as has been pointed out by Langmuir and Labrouste) a means of seeing whether the films were solid or liquid. In the solid films motes were not blown about by the air blast: in liquid films, motes moved about without difficulty.

Solidification occurred usually as soon as the film was formed on neutral solutions (at Q) and on acid solutions at or soon after the steep part of the curve was reached. Occasionally, however, there was some delay in solidification: this did not appear to affect the compressibility. In the steep part of the curves, apparently, the molecules are arranged so that they may form a solid film, though this may sometimes be delayed; in the less steep part the molecules are not capable of forming a rigid film. The probable difference in the arrangement of the molecules will be discussed later.

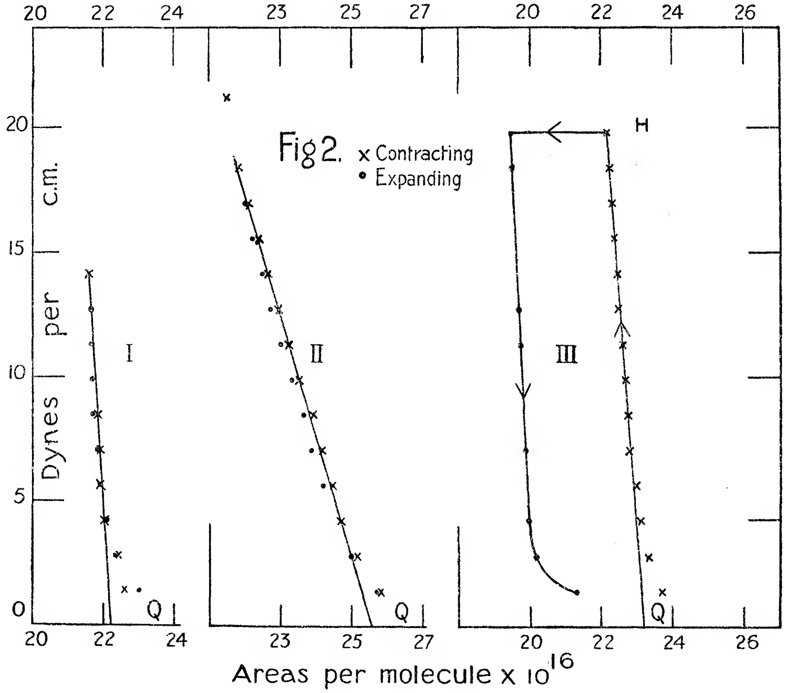
Absence of Hysteresis.

If the films below H are of 1 molecule in thickness, then there should be no hysteresis until collapse has set in. This was very nearly the case for the curves on neutral solutions and for the less steep portion on acid solutions. (Fig. 2, I and II.)

Films have also frequently been left under a compressive force for a long time, without change of area or any noticeable modification of properties. In one experiment the force was increased rapidly up to 15·5 dynes per centimetre, the film then left to itself for five hours, and the experiment then completed. The curve showed no discontinuity, although a change of 0·1 unit of area could have been detected.

This stability of the films showed the complete insolubility of palmitic acid in water; in the experiment just described not $\frac{1}{2}$ per cent. of the molecules left the film, although each one was in contact with an enormous excess of water.

The only sign of hysteresis noticed before the point H was reached was that when the compression was increased above about 20 dynes per centimetre the points on the curve of expansion sometimes fell at slightly smaller areas. The difference may have been due to the residual contamination in the film.



Influence of Dust Settling.

Providing the film was under compression about 14 dynes per centimetre, contamination settling from the air had no effect on its area. At pressures much lower than this there was a slow expansion.

This is of some importance, since it shows under what conditions the use of lycopodium or talc sprinkled on the surface may cause error, unless special precautions are taken to purify the powder from oily matter.

Form of Curves at very Low Compressions.

The linear relation holds accurately down to a force of 3 or 4 dynes per centimetre, but it is uncertain whether the film occupies a greater area of still lower compressions. Langmuir (footnote, p. 1889) indicates that the curves *may* become asymptotic to the axis; and most of my experiments showed a slight divergence from the straight lines at 1·4 dynes per centimetre. The amount of divergence could not be measured with certainty, however, and it seems doubtful if the method is yet refined enough to decide whether the effect is a property of the palmitic acid or is due to the correction for residual contamination being imperfectly known, or to traces of impurity in the acid.

Table II gives the area occupied by the film at no compression under the head "Corrected area," assuming the linear relation to hold throughout, at different concentrations of hydrion. Column 2 gives the observed areas per molecule without any correction for residual contamination, and column 4 the salts used to regulate the hydrion concentration. Each figure is the mean of four or more observations. The areas are believed to be accurate within 5 per cent.

Table II.—Areas of the Uncompressed Films.

P_H.	Observed area.	Corrected area.	Salts in solution usually *about* M/70.
1	26·1	25·1	N/10 HCl.
2·9 to 3·1	26·3	25·3	KH phthalate + HCl.
4·2 4·4	27·2*	25·4	KH phthalate + NaOH.
5 5·2	25·8	25·1	KH phthalate + NaOH.
6	23·1	22·1	KH_2PO_4 + NaOH.
7	22·2	21·2	KH_2PO_4 + NaOH.
8·5	21·6†	21	H_3BO_3, KCl, NaOH.

* The curves on phthalate solutions at P_H 4 diverged considerably from a straight line near the base, for a reason unknown.

† At 8·5 there were signs of solubility of the films, which would diminish the observed area.

Structure of the Films.

The theory of Langmuir and Devaux that the films are one molecule in thickness between Q and H, each molecule being oriented with the carboxyl group towards the water and the hydrocarbon chain normal to the surface, is completely confirmed by these experiments. Ample evidence of this structure has already been given by Langmuir (*loc. cit.*) and Harkins and his collaborators (9). It may be emphasised, however, that the observed area of about 22×10^{-16} sq. cm., which is nearly equal to the estimated cross section of the hydrocarbon chain, is very much too small to allow any considerable number of the molecules to be arranged otherwise than vertically in the film: while considerations of solubility indicate that the carboxyl group will be directed towards the water rather than the other end of the molecule.

The slight diminution in area between Q and H, with a compressibility 4·5 times that of paraffin in bulk, is consistent with the theory that the molecules are being forced somewhat closer together, as in a liquid under compression. Stereochemical considerations indicate that the carbon atoms are not vertically above one another, but are probably arranged helically, the angle between two successive valency linkages being normally 109°, but being capable of increase or decrease under stress. In the film, the chains may be straightened out, while in the compression of paraffin in bulk, the pressure is applied also to the ends of the chains and prevents elongation, so that the rather greater compressibility in the case of the film is not inconsistent with the view that the chains are being crowded laterally without other alteration in position.

For other substances also, the evidence in favour of the layer being one molecule thick rather than two, appears to be conclusive, although Marcelin (10), following a suggestion of Rayleigh (4), contends that a double layer is formed. One of the principal arguments for the existence of a second layer has been that the area at H is for many substances, such as oleic acid, about half the area at Q. This great apparent compressibility of a unimolecular film does not necessarily mean however that the molecules are being reduced in volume by one half, which would indicate a true compressibility so high as to be out of the question, but it can be explained by the molecules being attached to the water by one point at H and by two points at Q, an explanation which is beautifully supported by Langmuir's discovery that the ratio of areas at Q and H bears an extremely simple relation to the number of points of residual affinity in the molecule. Thus, for oleic acid, with two points of affinity, the ratio is 2 to 1, for saturated acids it is very much less, and for ricinoleic acid, which has three points or more, the ratio is much greater: and, further, the areas were found to be approximately the same for all these substances at H. Clearly, the explanation is that the film is one molecule thick throughout, but that the molecules occupy an area roughly proportional to the number of points in contact with the water, being finally attached probably by the carboxyl group only.

Other reasons also negative the possibility of a second layer. There is evidence, both from the kinetic theory of gases and from recent very beautiful experiments by Langmuir (11), (12), on condensation, evaporation, and adsorption, that the attractive forces about the molecule extend to a range of a very few Ångström units only. Since the upper limit of the first layer is probably about 20×10^{-8} cm. from the water, any molecules in the second layer will be well out of range of the attraction, and will therefore not affect the surface tension of the water. And even if the molecular attraction is supposed to extend farther than this, it would be necessary to postulate (i) that the effect of a molecule in the first layer is *nil* until the molecules in this layer are repelling one another; (ii) while, on the other hand, molecules in the second layer lower the surface tension in exact proportion to the number present; and (iii) that the effect of molecules beyond the second layer becomes suddenly negligible. Some such postulates seem to be unavoidable, and it is difficult to see how they could *all* be simultaneously consistent with any imaginable law of force round the molecule: nor does it seem probable that modifications, which could be introduced in the conception of the film by considering the thermal motions, would much simplify the law of force needed to account for a bimolecular layer.

Probably, however, little error is involved in neglecting the thermal movements. There is a fairly complete analogy between the films at the temperature of these experiments and a solid. The films frequently possessed rigidity, and the properties were found to be unchanged, under certain conditions, over a range of 30° C. But at a well defined temperature, as Labrouste has shown, they "melt," undergoing a considerable increase in area and becoming mobile. In solids, the space lattice can be determined without taking account of the vibrations, and it seems probable that the thermal movements (in a vertical direction at least) are so small that the relative positions of the long molecules is not thereby disturbed.

Theory of the Transformation on Acid Solutions.

The following is suggested tentatively. From the data of molecular volume studies, the approximate cross-section of the palmitic acid molecule may be estimated. The volume of CH_2 is 17·8 c.c. at the m.p. of the paraffins; dividing by the Avogadro number and the distance, $1{\cdot}52 \times 10^{-8}$ cm., between the carbon atoms in the diamond, which may be expected to be nearly the same as the distance between successive carbon atoms in a chain, since the linkages are of the same type, the cross section of the chain is found to be $19{\cdot}3 \times 10^{-16}$ sq. cm. This is in fair agreement with the observed area occupied by the acid on neutral solutions. It is therefore probable that the steep parts of the curves indicate a repulsion between hydrocarbon chains not $-COOH$ groups.

A COOH group has a molecular volume about 1·7 times that of a CH_2 group, according to the data collected by Le Bas ((13), pp. 18 and 140). The length of the $-COOH$ group in the direction of the chain is unknown, and therefore its cross section is uncertain: it is probably, however, somewhat larger than that of the hydrocarbon chains.

The greater area on acid solutions will then be due to repulsion occurring between COOH groups: the smaller area on neutral solutions to these groups being so arranged that the hydrocarbon chains can come into close contact.

Probably this arrangement is simply that adjacent molecules are immersed in the water to different depths,* so that the carboxyls do not lie in the same horizontal plane. On acid solutions the molecules rise in the water till all are at approximately the same depth, and therefore the carboxyls touch, the chains being forced farther apart so that they cannot interlock to give a solid film.† A strong lateral compression (as in the upper part of the curves on acid solutions) will naturally force the carboxyls down so that there is again close packing.

The chains pack closely on neutral solutions without external lateral compression because the attraction of water for —COOH groups increases with decrease in the hydrion concentration. There is independent evidence for this variation in attraction. The interfacial tension between water and fatty substances is less, the more alkaline the water, as was shown by Clowes (14) with strongly alkaline solutions, and recently by Peters and Hartridge (15) working near the neutral point. Oleic acid behaves similarly, and Dr. Peters informs me that benzene solutions of fatty acids also show the same phenomenon, which appears to be general for surfaces consisting of a layer of carboxyl groups oriented towards the water. It follows, from a well-known theorem of Dupré (see Hardy (5), 1912, p. 611), that the work gained when a layer of COOH groups approaches the water is greater for alkaline than for acid solutions. The chemical reaction between alkali and COOH would lead one to expect an effect in this direction.

The resistance of the hydrocarbon chains to immersion is clearly shown in the decreasing solubilities and increasing adsorption of fatty acids as the chains are lengthened: in any given acid then it is probable that increased attraction on the carboxyl groups will cause immersion to greater depths.

Solubility in Alkaline Solutions.

As the alkalinity increases, many of the chains become further immersed, though there is not much further alteration of the film's properties, since the chains are already closely packed at $P_H 5{\cdot}5$; finally, the point is reached at which some molecules are completely immersed and solution commences. At this point the arrangement of minimum potential energy, in which the attractions are as completely satisfied as possible, will be that of aggregates having the carboxyl group outwards and the hydrocarbon chains packed in the centre. These will have a high molecular weight, and will probably carry many negative charges owing to the dissociation of the carboxyl groups.

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* This idea was suggested to me in conversation by Dr. Peters.

† More recent experiments on other substances indicate that close contact of long hydrocarbon chains is probably not a necessary or sufficient condition for solidity of the films.

The genesis of the "ionic micelles" in aqueous soap solutions, which have been recently studied by McBain and his collaborators (16), thus becomes clear.

The film dissolved so fast that measurements of compression were impossible, at a P_H of 10; at 8·5 the curve showed signs of solubility, and at 8 (at room temperature), solution was too slow to measure. I hope to obtain detailed measurements of the rates of solution under various conditions later.

Influence of Acidity on the Melting Point of the Films.

The effect of rising temperature is being studied, and the fact noted by Labrouste (*loc. cit.*) that at a fairly well-defined temperature the films increase greatly in area under low compressions, and (if previously solid) become liquid, has been confirmed. It is striking, however, that a much higher temperature is required to melt the films on alkaline solutions than on acid, a fact which confirms the theory that the molecules are attracted more firmly to the water in the former case. Table III gives the approximate temperatures at which the first change occurs in the films.

Table III.

P_H.	Approximate m.p.	P_H.	Approximate m.p.
(1)	(25° C.)	(6)	(38°)
3	25°	(6·5)	(40°)
(5)	(33°)	8	Above 50°
(5·5)	(33°)		

Figures in brackets are provisional only.

Nature of the Collapse at H.

Fig. 2, III, shows the hysteresis effect observed after the collapse had proceeded a short distance. The curve of expansion was approximately parallel to the curve of compression of the original undamaged film, and this considered together with the facts that solid particles become visible after it is passed, and that solid palmitic acid does not spread upon water, indicates that the mechanism of the collapse was the destruction of a part of the surface film, molecules being ejected to form aggregates of relatively great thickness, the remainder of the film being unaltered in properties.

The solid films most frequently collapsed in the manner described by

Labrouste (*loc. cit.*), with the appearance of solid material in the form of very fine lines on the surface, roughly, arcs of circles extending from one end of the barrier to the other. Occasionally, however, the solid appeared in flakes, not lines, and when this occurred the flakes were usually, though not invariably, close to the air blasts.

Collapse, once started, sometimes proceeded to very small areas without further weights being required, the glass barrier being moved up slowly so as to keep the balance float nearly at zero. More often there were checks, frequently several in one experiment at irregular intervals, to overcome which the forces had to be increased by an amount indefinite, but occasionally nearly as high as the force given for H by Langmuir. When complete checks occurred, it was often possible to increase the force by a considerable amount before collapse set in again: and in these cases the curve would rise at the check at about the same slope as the curve of the original film, as would be expected if the resistance were due to an intact portion of the film with its original properties.

As might be expected from the diminished attraction on the $-COOH$ groups, the *minimum* force at H observed on acid solutions was less than that for neutral solutions, being sometimes as low as 16 dynes per centimetre (fig. 1, IV).

The nature of the collapse is easily accounted for. A single molecule leaving the film must overcome the attraction of the carboxyl group for the water, and also that of the hydrocarbon chain for its neighbours. The surface tension of paraffins and their solubility in one another indicates that this attraction is important.

If, however, a group of adjacent molecules are ejected together, the only work done is that of the carboxyl groups against the attraction of the water. Hence the film will collapse at comparatively few points only, and the solid flakes or lines on the surface are to be expected.

The metastable state and the checks to collapse are explained probably by the necessity of some nucleus for starting expulsion of the molecules at any point. Possibly these are dust particles, which have fallen on the surface before, or during, the application of the film, or at very low compressions, and have become incorporated with the film. The checks indicate that a nucleus in one part of a solid film may be useless for more than a certain number of molecules, being very likely expelled along with them.

Explanation of Langmuir's Curves on Acid Solutions.

The very sharp rise in resistance to compression shown at areas from 2 to 8×10^{-16} sq. cm. per molecule, is, I am sure, only an instance of a similar check to collapse, and is due to the same cause (*loc. cit.*, figs. 10, 11, 12, 17). The areas at which these occur are much smaller than the cross section of any part of the molecules, and the effect is therefore very unlikely to be a property of an entire unimolecular film in any condition; and moreover, in numerous experiments, I have not observed any regularity in the phenomenon. It sometimes occurs on neutral solutions, as well as on acid; it does not invariably occur even on the latter; it may occur at any area after solidification of the film; and frequently there are several partial checks, at different areas, in one experiment.

The checks may be due to exhaustion of the nuclei available in the film, so that the remaining parts of the film, having no nuclei or less effective ones, are more resistant to collapse.

I should like to express my thanks to Mr. W. B. Hardy, F.R.S., for valuable advice during the progress of this work, and to Miss Jordan Lloyd for very kindly doing the electrometric determinations. The experiments were done in the Chemical and Biochemical Laboratories, Cambridge, and are being continued.

Summary.

1. A modification of the technique for examining the properties of thin films of substances on water is described, special attention being given to the avoidance of leaks past the confining barriers and to correcting for the residual contamination on the water which cannot be wholly avoided.

2. Experiments on palmitic acid confirm Langmuir's results in general. The curves of compressibility of the films are accurately straight lines, except for a possible doubtful deviation at very low compressions.

3. The film changes abruptly in properties at a hydrogen ion concentration about 10^{-5} N. The change is confined to films under compression less than about 16 dynes per cm. The area occupied by each molecule becomes about 20 per cent. greater than on neutral solutions.

4. Langmuir's view that the films consist of a single layer of molecules, oriented with their carboxyl groups towards the water, is confirmed and extended. Probably the hydrocarbon chains are tightly packed on neutral solutions, adjacent molecules being drawn into the water to different depths. On neutral solutions the molecules rise in the water so that the $-COOH$ groups, which are probably of greater cross section than the chains, are in contact with each other. This arrangement gives a liquid film, whereas the packed hydrocarbon chains normally give a solid one. There is independent evidence of an increased attraction of water for $-COOH$ groups with increasing alkalinity.

5. The formation of the "ionic micelle" of soap, as the film dissolves in more alkaline liquids, is a simple consequence of the increased attraction on the carboxyl groups and the attraction of the chains for each other.

6. Hysteresis in the unimolecular films of palmitic acid is absent or extremely small in amount, at room temperature.

7. Palmitic acid is completely insoluble in water slightly on the acid side of neutrality, the films preserving their area and properties unchanged for hours.

8. Compression beyond a certain point causes collapse of the film: the ejected molecules forming aggregates visible to the naked eye. The remainder of the film appears to be unchanged in properties. Different films, and even different parts of the same film, vary very much in their resistance to collapse. The collapse seems to be aided by nuclei, the nature of which can only be conjectured at present.

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